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Oxygen intercalation and intergranular coupling in the 110-K $Bi_{1.7}Pb_{0.3}Sr_{1.8}Ca_2Cu_{2.8}O_{9.45+\delta}$ superconductor

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The effect of the carrier-density variation on the crystal structure and properties of $Bi_{1.7}Pb_{0.3}Sr_{1.8}Ca_2Cu_{2.8}O_{9.45+\delta}$ was studied by controlling the oxygen content. The kinetics of oxygen sorption are found to depend on the temperature and the partial pressure of oxygen during annealing. Also the oxygen trade is exactly reversible. The hole concentration p in the $[CuO]^{+p}$ sheets changes from 0.188 to 0.312 holes/CuO by heat treatment of the superconducting samples at appropriate oxygen partial pressures. The c parameter also decreases by 0.2% with variation of the hole concentration in this range. The high-T_c phase is also found to be stable against the reannealing process. However, two additional peaks are observed in the x-ray-diffraction patterns of all samples which depend only on the oxygen content. The change in the critical temperature due to the hole concentration is similar to other p-type high-T_c cuprates. The intragranular transition and the Josephson phase locking temperature determined from ac-susceptibility measurements correspond to the midpoint temperature of resistivity transition and zero-resistivity temperature, respectively. Although the intragranular transition temperature changes in a range of 2.5 K, the intergranular coupling is much more sensitive to the chemical modification in CuO sheets and it varies in a range of 40 K. With oxygen intercalation, the Josephson phase locking temperature of intergrain junctions approaches that of the intragrain value and the maximum value of T_c. This result suggests that the anionic vacancies at grain boundaries play a special role in the Josephson coupling.

I. INTRODUCTION

The crystal structure of copper oxide superconductors is basically formed by the intergrowth of oxygen deficient perovskite layers ($A'CuO_{3+x}$) with insulating rock salt-type AO planes. The oxidation of antiferromagnetic $[CuO]^{+p}$ sheets leads to superconductivity in these compounds. The charge-carrier concentration that is determined by the overall chemistry of the system controls the superconducting transition temperature. The amount of charge transfer between the conduction layer and the charge reservoir depends on the structure and also the oxidation states of the metal cations.[1] Therefore, the charge concentration can be varied by the chemical modification of the active CuO layer or adjacent layers by the addition or removal of oxygen[2–4] and/or by the metal cation substitution.[5–7] Le Page *et al.* observed that the insertion of extra oxygen in the Bi layers causes the incommensurate modulation in the structure of the 2:2:1:2 phase.[8] It has been demonstrated that the modulation has significant effects on the band structure and the extra oxygen causes distortion producing the electronic carriers (holes or Cu^{+3}) in CuO sheets.[9] Detailed bond-length studies in the double layer Bi superconductors resulted in that the Bi valency is less than +3 (Ref. 10). This reduction reveals that the BiO layers are acting as hole reservoirs. The transition temperature has been observed to be sensitive to the oxygen stoichiometry in bulk[2,4] and in thin-film[11] samples of 110-K Bi superconductors. However, the correlation between the transport properties and the crystal structure with different hole concentrations has not been well established because of the difficulties in preparing thermodynamically stable samples.

The transport properties are very much affected by the granular microstructure of high-T_c ceramic superconductors.[12] Dimos *et al.*[13] demonstrated a strong dependence of the critical current density at artificial grain boundaries of $YBa_2Cu_3O_{7-\delta}$ (YBCO) and, furthermore, that grain boundaries with tilt angles larger than 3°–5° act like SNS-type Josephson junctions.[14] Deutscher and Müller showed, in particular, how planar defects should behave as Josephson junctions with a depressed order parameter when the coherence length is in the order of interatomic distances.[15] The degree of order-parameter depression is very sensitive to the boundary crystallography. The energy dispersive x-ray analysis (EDX) in the scanning transmission-electron microscope showed that the composition varies within a boundary and from boundary to boundary.[16]

It was the aim of the present work to investigate the influence of oxygen sorption on the hole concentration, the crystal structure, and the transport properties of 110-K Bi superconductors. A series of samples was prepared by annealing at different oxygen partial pressures. The high-T_c phase of the samples was found to be

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thermodynamically stable and allows the accommodation of nonideal oxygen stoichiometries. The formal copper valency varied between 2.188(2) and 2.312(4) as determined by chemical titration. From the analysis of x-ray-diffraction (XRD) data and formal copper valency values, it has been found that the oxygen sorption creates a structural modification in the samples. In the overoxidation region, this modification becomes important and the *c* parameter sharply decreases. The critical parameters of granular samples were deduced by ac susceptibility measurements. The transition temperature is dependent on the hole concentration and its variation is determined for other *p*-type superconductors, but the intergranular phase coherence is greatly affected by oxygen content. The results of ac susceptibility measurements were discussed on the basis of the effect of the anionic vacancy ordering at grain boundaries.

II. EXPERIMENT

Samples of nominal compositions of $Bi_{1.7}Pb_{0.3}Sr_{1.8}Ca_2Cu_{2.8}O_{9.45+\delta}$ were prepared by firing the required quantities of well-mixed Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, and CuO powders at 800 °C for 24 h. The product was ground, pelletized, and sintered at 845 °C for 416 h with a few intermediate grindings. All the samples were characterized by XRD using Ni filtered Cu $K\alpha$ radiation. The average formal oxidation state of copper was obtained by Fe^{2+}—$Cr_2O_7^{2-}$ titration. All the experiments were run in Ar ambient, and the hole concentration was calculated with a relative error of 0.25%. Thermogravimetric measurements were carried out with a Dupont series 9000 thermal analysis system in different atmospheres. The electrical resistivity measurements on sintered pellets were made with a standard four-probe technique using an ac measuring current of 1 mA at 16 Hz. The ac susceptibilities of the samples were measured by a LR 400 mutual inductance bridge with a precision of 10^{-7} emu. The amplitude of the excitation field was 56 mOe, and the frequency of the field was 16 Hz.

III. RESULTS

The ac electrical resistivity measurements on the starting sample as well as on the annealed samples showed that the physical properties are reversible with changing oxygen content (Fig. 1). The room-temperature resistivity of the starting sample is 1.7 mΩ cm. The onset of superconductivity starts at 112 K and zero resistivity temperature (T_{c0}) is 103 K. The XRD pattern of the sample [Fig. 4(a)] indicates a single superconducting phase ($n=3$) with the lattice constants of $a=5.398(3)$ Å, $b=5.392(3)$ Å, and $c=37.09(2)$ Å. This sample was annealed again at 845 °C for 4 h under air and then quenched to room temperature in air. The room-temperature resistivity of the air-quenched sample increased to 13.2 mΩ cm. The resistance versus temperature curve shows semiconducting behavior down to 120 K where the superconducting transition begins and zero resistance is reached at 80 K. No other phases with lower T_c and no line splitting were observed in the XRD pattern of the quenched sample. This sample was reannealed under air at 845 °C for 4 h, then furnace cooled to room temperature at an approximate rate of 200 °C/h. After this heat treatment, the zero resistance temperature rose to 102.5 K. In the normal state, the metallic behavior of the sample remained as that of the starting sample, although its room-temperature resistivity was two times larger than the latter. The *c* parameter increased from 37.09(3) to 37.17(4) Å after the starting sample was quenched from 845 °C to room temperature in air. The basal plane parameters remain approximately the same within the accuracy of the measurement while the *c* parameter changes. These observations clearly demonstrate that the oxygen content controls the transition temperature as well as the *c* parameter. Hence, the lattice expands with oxygen unloading as in YBCO. To determine the amount of oxygen loss in the air-quenched sample, thermogravimetric analysis was done. The sample was heated up to 845 °C and then cooled down to the room temperature at a rate of 10 °C/min under oxygen atmosphere. After this thermal cycle, the weight of the sample increased by 0.16%, which corresponds to nearly 0.1 oxygen atoms per formula unit, and the zero resistance temperature shifted from 80 to 102.5 K. This oxygen uptake of 0.1 atoms per formula unit diminishes the *c* parameter to 37.10(3) Å.

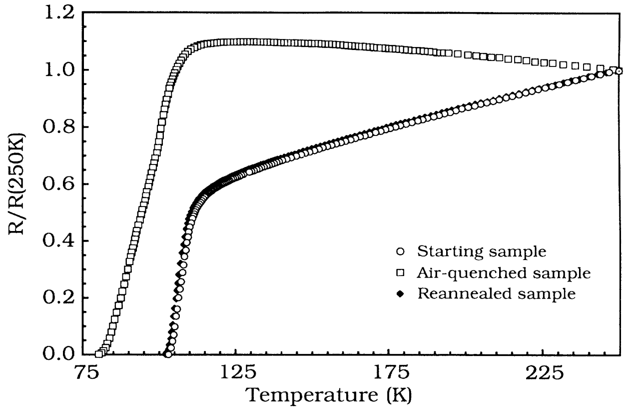

FIG. 1. Reversible electrical resistivity behavior in the starting sample depending on the thermal annealing procedure. The starting sample was annealed at 845 °C for 4 h in air and then air-quenched to room temperature. The annealed sample was reheated at 845 °C for 4 h and then furnace cooled to room temperature at an approximate rate of 200 °C/h.

The oxygen dependency of the weight variation was investigated by thermogravimetric analysis (TGA) experiments in different atmospheres. The starting sample was heated up to 780 °C and subsequently cooled at a rate of 10 °C/min under argon flow. After this reducing treatment, the oxygen loss was 0.25 atoms per formula unit. However, the sample was still superconducting, and the XRD pattern showed a single phase with 110 K transition temperature. Reheating of the sample up to 845 °C was followed by a cooling process, first in air and then in oxygen. Through these thermal cycles, the oxygen uptake per formula unit were 0.12 atoms under air and 0.13

atoms under oxygen. Figure 2 shows the resulting TGA trace. Note that the oxygen loss and sorption are reversible but small; 0.25 oxygen atoms as compared to the 0.9 for YBCO. The T_{c0} of the sample also changed reversibly after this treatment; it became 103 K, as for the starting sample. The TGA trace shows also that the oxygen intercalation increases with rising temperature. The oxygen sorption under air reaches a maximum value of 0.23 atoms per formula unit at nearly 800 °C. However, the oxygen sorption per formula unit is 0.38 under oxygen atmosphere, while the sample adsorbed 0.12 atoms of oxygen under air. These results indicate that the influence of oxygen sorption on the annealing temperature is also a function of the oxygen partial pressure.

The Cu valence and the oxygen content of the starting sample have been measured by thermogravimetric analysis (TGA) under a reducing atmosphere (H_2) and also by chemical titration. The redox titration using the Fe(II)–Fe(III) couple was done in an Ar atmosphere to prevent the contribution of any dissolved oxygen. Also, the change of the reaction potential was followed by a saturated calomel electrode versus a Pt electrode and the formal copper valency in the starting sample was calculated as 2.215(3). The TGA trace obtained for the sample is shown in Fig. 3. The hydrogen reduction was completed at nearly 520 °C and this value is smaller than the observed values.[5] Although the determination of the temperature at which the reduction is completed is straightforward, the calculation of the oxygen content from TGA data is not so simple. The reason for this problem stems from the formation of a second oxide phase, which was determined to be Cu_2O by an XRD pattern of the reduced phase. The accuracy of these techniques is limited by difficulties in determining the exact elemental compositions of the reacting compounds, because of the existence of a minor phase in the form of $Bi_{0.09}Sr_{0.17}Ca_{1.83}Cu_{0.80}O_{3.00}$ as determined by EDX analysis in the scanning electron microscope (SEM). The physical properties are unaffected by this phase, since it is in the form of isolated inclusions that comprise 2–5 % of the total volume. A weak reflection of $2\theta=36.4°$ in Fig. 4 was attributed to this phase.[17] The oxygen content of the sample determined by chemical analysis is slightly higher than the results of the TGA data. Chemical titration gave an oxygen content of 9.751(3), while TGA indicated 9.68(6) per formula unit of $Bi_{1.7}Pb_{0.3}Sr_{1.8}Ca_2Cu_{2.8}O_{9.45+\delta}$. These values are in agreement within the experimental error.

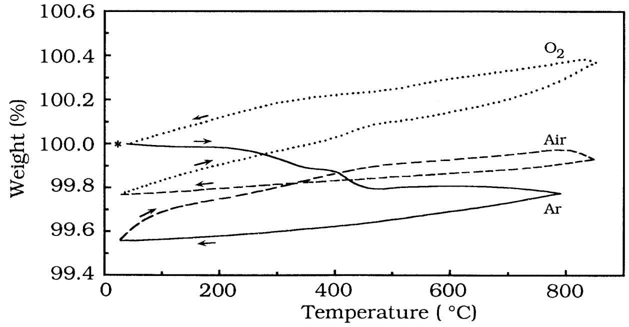

FIG. 2. Thermogravimetric measurements for the starting sample performed by heating and cooling in argon (solid line), then reheating and cooling first in air (dashed line) and second, in oxygen (dotted line) under normal pressure conditions. The asterisk shows the start of the cycle, and arrows denote the thermal annealing direction of the sample.

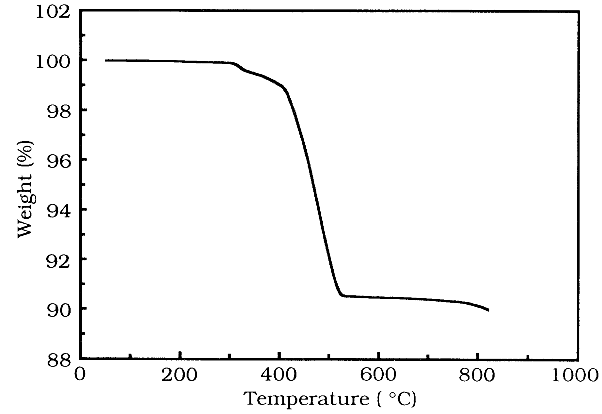

FIG. 3. TGA trace of the sample showing the weight loss due to reduction by heating up to 845 °C at a rate of 10 °C/min under hydrogen.

TGA experiments in different atmospheres showed that the superconducting phase is sensitive to the oxygen partial pressure during thermal annealing. To study the effects of oxygen on the crystal structure and physical properties, the starting sample was equilibrated under oxygen pressures of 15, 35, 65, 90, and 110 mbar at 750 °C for 12 h and then furnace cooled to room temperature. The hole concentration p in the $[CuO]^{+p}$ sheets was determined by chemical analysis. Depending on the oxidation state of the CuO sheets, the hole concentration increases from 0.188(2) to 0.312(4) holes/CuO while the oxygen partial pressure changes from 15 to 110 mbar. This behavior shows that p increases with oxygen partial pressure while the temperature is kept constant. The hole concentrations of the samples annealed at 845 °C (1000 mbar), and 750 °C (90 mbar) were found to be 0.296(3) and 0.309(4) holes/CuO, respectively. Therefore, the preparation of the samples which have nearly the same p values could be possible by shifting the applied oxygen partial pressure P to higher values with increasing annealing temperature T. This behavior is also expected from the $\ln[P/(aT^{5/2})]$ term of the chemical-potential equation.[18]

The oxygen uptake causes changes in the x-ray-diffraction patterns of the samples. Two additional peaks were observed at $2\theta=17.89°$ and $2\theta=31.31°$, and these peaks became stronger with increasing electron deficiency in the CuO sheets (Fig. 4). Actually, these peaks were also recorded for the starting sample as extremely weak reflections [inset of Fig. 4(a)]. They cannot be connected with the minor phase $(Sr,Ca)_2CuO_3$, since the intensity of the 36.4° peak corresponding to this phase stays unchanged by oxygen uptake. Besides, no significant changes in the nominal compositions of the superconducting and minor phase grains were observed by EDX analysis. However, these peaks could be related to the impurity phase, Ca_2PbO_4, which has thermodynamic stability in this system. The (101) and (103) planes of this structure reflect x rays at $2\theta = 17.74°$ and $2\theta = 31.55°$, respectively. SEM-EDX analysis gave no evidence for the nucleation of this phase but it may segregate in the grain boundaries with the oxidation of Pb^{2+} to Pb^{4+}. Furthermore, the existence of the Pb-rich amorphous phase in the grain boundaries has been observed by the high-resolution electron microscope[19] and this phase may crystallize in the form of Ca_2PbO_4 by oxygen uptake. If this were the case, one would expect to have additional x-ray-diffraction peaks other than those observed. The Ca_2PbO_4 phase has a strong peak at $2\theta = 31.96°$, which is also the location of (119) reflection for the high-T_c phase. However, there is no significant variation in the intensity of this reflection with oxygen uptake. In case of a new phase formation, the oxygen trade in the sample would be expected to be irreversible. However, as mentioned before, TGA experiments showed that the oxygen content can be controlled in a reversible and systematic way by changing the oxygen partial pressure. These observations give no evidence for the destabilization of the 2:2:2:3 phase by oxygenation. The additional peaks must belong to the high-T_c phase. They were well attributed to the (013) and $(01\underline{11})$ reflections of the orthorhombic 2:2:2:3 phase. As is clearly seen in Fig. 4, these peaks and in addition, the (002) and $(00\underline{10})$ reflections, are oxygen content dependent. Hence, it is concluded that the intensity variation of these reflections is caused by chemical ordering in the crystal structure of the 110-K phase with oxygen uptake.

The c parameter exhibits a significant change with p, dominantly for $p > 0.25$ holes/CuO that is the result of the modification in the crystal structure (Fig. 5). This indicates that the interlayer spacing decreases with the increasing electron deficiency in CuO sheets as observed in the other perovskite structures. The c parameter decreases by 0.2% with the increase of formal copper valency from 2.188(2) to 2.312(4) and the volume change is caused primarily by the variation of the c parameter. The volume change on oxygen sorption is 2.5 times smaller than that of YBaCuO for the same interval of hole concentration.[20] With the addition of holes to the CuO

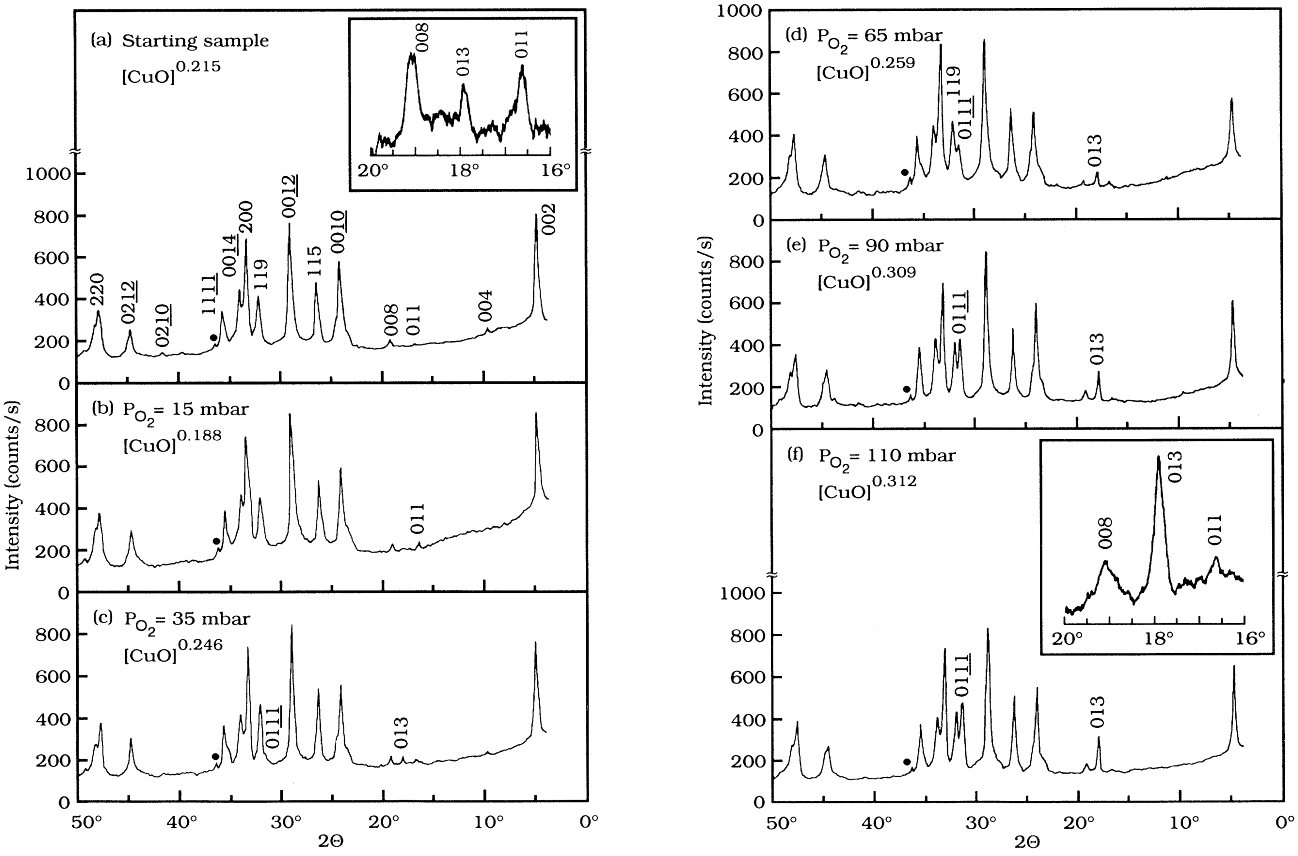

FIG. 4. The x-ray-diffraction pattern of the samples reannealed at 750 °C for 12 h under different oxygen partial pressures. The reflections are indexed with respect to the space group $Am2a$. The insets magnify the region between 16° and 20° for two samples. (●) the minor insulator phase.

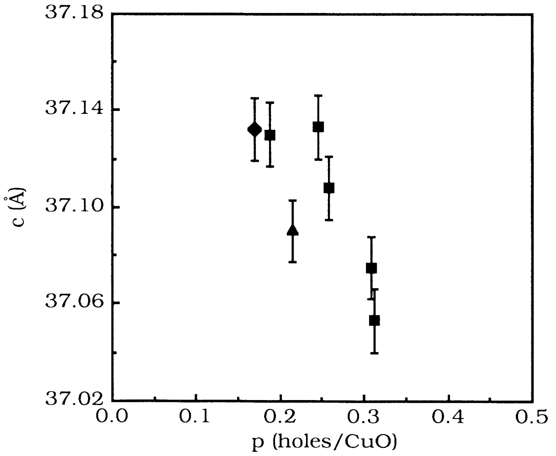

FIG. 5. The variation of the *c* parameter depending on the hole concentration. (▲) the starting sample; (◆) the slowly cooled sample with a rate of 100 °C/h under air.

sheets, the variation of the basal plane parameters is undetectable within our experimental resolution.

The effects of the chemical modification on the critical parameters were investigated by ac susceptibility and electrical resistivity measurements. The real part of the ac susceptibility $\chi'(T)$ shows a two-stage behavior due to phase coherence in the grains and between grains as seen in Fig. 6(a). The granular microstructure of the samples strongly influences the physical properties. The intragrain transition and the intergranular phase locking temperatures are denoted by T_c and T_j, respectively. T_c is defined as the inflection point of the high-temperature transition of $\chi'(T)$. T_j is the temperature where the imaginary part of susceptibility increases from zero and it also corresponds to the onset of the low-temperature transition. The imaginary part $\chi''(T)$ exhibits an intergranular loss peak and it starts at T_j since the applied field strength is greater than the Josephson lower critical field. On the other hand, intragranular loss peak was not observed for the fields up to 12.23 Oe, indicating that the intragranular lower critical field of the reannealed samples is greater than 12.23 Oe at about 107 K.

The hole concentration dependence of T_c and T_j is given in Fig. 7. By increasing the hole concentration, these critical temperatures increase and then pass through the maximum points at around $p = 0.26$ holes/CuO and then fall down. This behavior is in agreement with other *p*-type copper oxide-based superconductors. In the same figure, midpoint temperature (T_m) and zero resistivity temperature (T_{c0}) calculated from the normalized resistance curve [Fig. 6(b)] are shown for various hole concentrations. This comparison is informative. The midpoint temperatures of the resistivity transition are very close to the intragrain diamagnetic transition temperatures and also zero resistivity temperatures are nearly the same as the intergrain coupling temperatures. The disagreement between these compared temperatures in some samples originates from the difficulty in the description of them and the inhomogeneity in the intragrain and intergrain coupling energies.[21] In high-T_c superconductors, the coherence length of superconducting pairs is extremely small [$\xi_{GL}(0) \cong 20$ Å] (Ref. 22) and the diamagnetic shielding will strongly feel inhomogeneities in local hole concentration at the grain boundaries and within grains. This is caused by the local weakening of superconductivity that controls the elementary flux-pinning interaction. The large width of the diamagnetic transitions and especially the small third transition near 50 K in high-T_j samples indicate the existence of inhomogeneities in intragrain and intergrain coupling energies [Fig. 6(a)]. In Bi cuprates, the exact nature of cationic nonstoichiometry[10] creates a local variation in the oxygen content. Therefore, a uniform oxygen stoichiometry in the samples is not expected. The width of intragranular transition [inset of Fig. 6(a)] is increased only in the overoxidation region due to the increased inhomogeneity in oxygen content of the grains. On the other side, the oxygen content influences the magnitude of the small intergranular transition and the diamagnetic

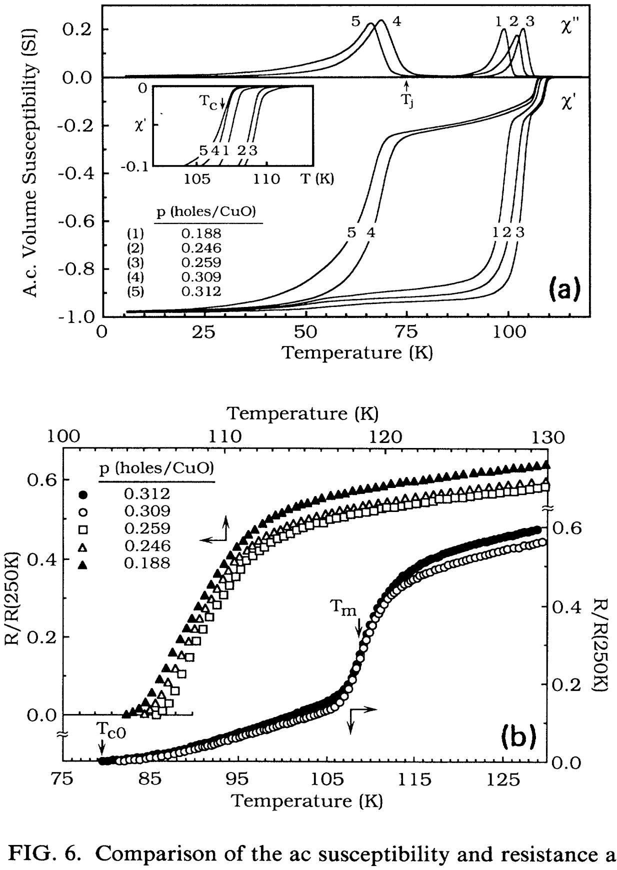

FIG. 6. Comparison of the ac susceptibility and resistance as a function of temperature. (a) The hole concentration dependence of the imaginary part (χ'') and the real part (χ') of ac susceptibilities at 56 mOe. The inset shows an enlarged area of χ' between 0.0 and -0.1; (b) the normalized resistance of the samples. The midpoint temperature of resistance (T_m), the intragrain transition (T_c), and intergrain phase locking temperatures (T_j), are identified in the figures for the sample whose hole concentration is 0.312 holes/CuO.

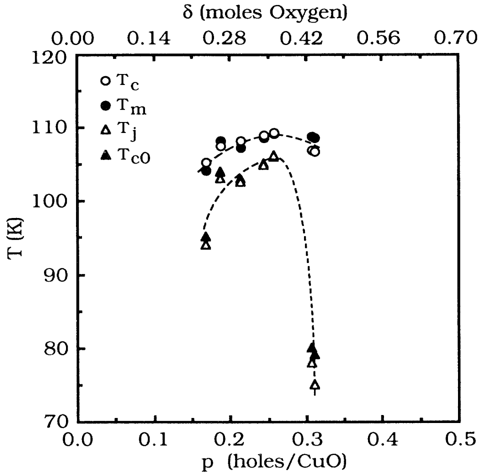

FIG. 7. Dependence of critical parameters on the hole concentration p and the excess oxygen δ in $Bi_{1.7}Pb_{0.3}Sr_{1.8}Ca_{2.8}O_{9.45+\delta}$. T_c, T_j, T_m, and T_{c0} stand for intragrain transition, Josephson phase locking, midpoint, and zero resistivity temperatures, respectively. The lines are guides to the eye.

shielding at high temperatures approaches the perfect value -1 with increasing oxygen content in the lower oxidation region. Therefore, the difference between T_j and T_{c0} reduces as a consequence of the growing fraction of high-T_c superconducting junctions and decreasing inhomogeneity due to oxygen at grain boundaries. At higher oxidation levels, the midpoint temperature shows a small change due to the small decrease in the intragrain transition temperature. However, the zero resistivity temperature drastically shifts toward lower temperature by forming a tail due to the sharp decrease in the Josephson phase locking temperature. The difference between T_j and T_{c0} grows with increasing inhomogeneity in local hole concentration at the intergranular region. The value of T_{c0} is determined by T_j and the quality of intergrain coupling is as expected because the sample will have zero resistivity if there is a completed percolation path due to Josephson coupling between the grains.[21]

By increasing the hole concentration, the Josephson phase locking temperature T_j approaches the intragrain transition temperature T_c in the lower oxidation region and the difference between T_c and T_j shows a similar behavior to the resistivity in the normal state. The resistivity at 250 K (Fig. 8) of the samples decreases monotonically with p and reaches its minimum value as does $T_c - T_j$. Increasing the electron deficiency in CuO sheets continuously improves the conductivity and raises the Josephson phase locking temperature at grain boundaries. However, higher levels of oxidation result in a sharp increase in $T_c - T_j$ and enhance the normal-state resistivity. In $La_{2-x}Sr_xCuO_4$ samples, Torrance *et al.*[23] observed that the conductivity continues to improve while superconductivity disappears at high hole concentrations. However, the resistivity measurements of the samples which have poor intergranular coupling showed that the conductivity decreases after its maximum value.[24] The normal-state resistivity of granular samples was determined by the resistivity of the junctions. The decreasing resistivity down to its minimum value indicates a reduction of the grain-boundary resistance. If the scattering mechanism does not change due to the oxidation state in CuO planes, the carrier concentration in the grain boundaries increases with bulk hole concentration. However, the behavior of normal-state resistivity and the sharp decrease in the Josephson phase locking temperature indicate that percolation and flux-pinning mechanisms change and have different characteristics in both the lower and overoxidation regions.

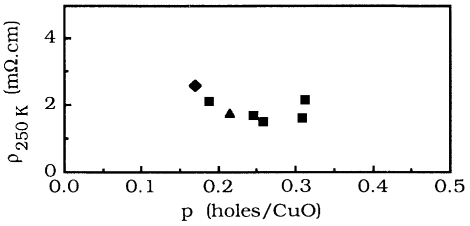

FIG. 8. The correlations between the hole concentration and the normal-state resistivity at 250 K. (▲) the starting sample; (◆) the slowly cooled sample.

IV. DISCUSSION

A. Excess oxygen

The prepared high-T_c phase was greatly affected by oxygen content and the formal copper valency could be changed from 2.188(2) to 2.312(4) by controlling the oxygen content of the samples. The oxygen uptake created a significant variation in the XRD pattern of the samples. A minor change in the intensity of the (002) and $(00\underline{10})$ reflections and two additional peaks were observed. The intensity of the additional reflections became stronger with increasing oxygen content. These additional peaks were well attributed to (013) and $(01\underline{11})$ reflections corresponding to the high-T_c orthorhombic phase. The (013) peak at $2\theta = 17.89°$ had been indexed to Ca_2PbO_4 or an unknown phase by some authors.[25,26] However, we showed that the oxygen content of our samples can be changed reversibly and the formation of a new phase is unexpected. The oxygen content also controls the c parameter and the c parameter decreases depending on the Jahn-Teller distortions with rising formal copper valency. These results reveal that the prepared high-T_c phase has the thermodynamic stability and there is a chemical modification in the structure by increasing the excess oxygen content. This rearrangement does not alter the space group since the additional peaks observed in the starting sample have extremely weak intensities. If (011), (013), and $(01\underline{11})$ peaks are ignored, the reflections with the indices of $hkl(k+l=2n+1)$, $hk0(h,k=2n+1)$, and $0kl(k,l=2n+1)$ disappear in accordance with the extinction rule. This means that the space group for the average structure of the high-T_c phase is *Amma* which is equivalent to noncentrosymmetric *A*2*aa* in the literature.[27–30] The satellite $0kl$ reflections as (011) were observed in space-group studies but their effects were not considered in the Rietveld analysis.[27,30] The hole concentrations of the samples used in these investigations were unknown and we observed that the additional reflections become stronger, if the hole concentration is greater than 0.24 holes/CuO. The XRD pattern of the sample which was obtained under 110 mbar O_2 partial pressure shows (013) and $(01\underline{11})$ reflections so clearly that they cannot be ignored any longer. The observed $0kl$ reflections fulfill the general condition $k+l=2n+1$. In this case, the space group of the prepared high-T_c phase may be noncentrosymmetric $Am2a$ or $Am2m$.

The occurrence of oxygen atoms as a possible reason for the existence of the modulation was proposed by Le Page *et al.*[8] The systematic increase of modulation spacing is related to the systematic decrease in the excess oxygen content in the BiO layers. The observed modulation for some $Bi_{1.75}Pb_{0.25}Sr_2Ca_2Cu_2O_{10+\delta}$ samples is $7.12b$ Å (Ref. 31) and this corresponds to an excess oxygen concentration of $1/7.12=0.140$ atoms per formula unit. The excess oxygen content of our samples is greater than this value. The excess oxygen per formula unit for the starting sample ($Cu^{2.215+}$) is 0.301(4) atoms. This value is 0.437(4) atoms for the sample ($Cu^{2.312+}$) which was annealed at 110 mbar O_2 partial pressure. X-ray microprobe analysis[31] and the refinement of the population parameters from neutron and x-ray data[27–29] revealed the presence of Pb in Ca positions and the occupancy of Sr sites by Ca and Bi ions. The excess oxygen is intercalated into the BiO layers in order to compensate for the cationic charge imbalance resulting from wrong site occupations.[31] Large scale EDX studies showed that there were 3% local deviations from the nominal composition of $(Bi,Pb)_{2.1}Sr_2Ca_2Cu_{2.9}O_x$ in the superconducting phase of the sample under investigation. The charge imbalance of the lattice is increased by the presence of Bi and Pb ions at the Cu sites and there is only one way for the charge compensation and that is anion uptake.

B. Intergranular coupling

The influence of the hole concentration on the transition temperatures is similar to other p-type high-T_c superconductors.[32] The influence of the hole concentration on the intragrain transition and on the intergrain phase locking temperatures has different aspects. The intragrain transition temperature is not very sensitive to the electron deficiency in CuO planes between 0.188(2) and 0.312(4) holes/CuO. For the 110-K phase, the hole concentration corresponding to the maximum value of T_c was predicted to be 0.25 holes/CuO by Rao and coworkers.[33] In this study, we observed that T_c gives a maximum value at 109.3 K for $p=0.259$ holes/CuO. The variation of the intragrain transition temperature is in a range of 2.5 K. However, the intergrain phase locking temperature varying in a range of 40 K is strongly correlated with the oxidation states in CuO planes and this sensitivity can be understood by anionic vacancy ordering phenomena at the intergrain region. The oxygen diffusion is more rapid at grain boundaries than in the crystalline lattice so that the composition of the grain boundaries equilibrates more rapidly than that of the bulk. The decrease of the anionic vacancy concentration with the oxygen partial pressure is faster at grain boundaries than within grains. In this case, one would expect that the intergranular phase coherence becomes stronger and the diamagnetic shielding at high temperatures increases and approaches the perfect diamagnetic value due to the decrease of anionic vacancy concentration. Therefore, the effective hole concentration at grain boundaries continues to improve in the lower oxidation region and the Josephson phase locking temperature moves to high temperatures according to the universal correlation of T_c.

The carrier concentration in the interface region is smaller than in bulk because of the order-parameter depression. Therefore, if the percolation characteristics do not change, the carrier concentration in the grain boundaries is enhanced with increasing hole concentration. At high oxidation levels, the sharp decrease in the Josephson phase locking temperature and the behavior of normal-state resistivity indicate that the percolation mechanism and flux-pinning dynamics at grain boundaries change. In addition, the inhomogeneities at grain boundaries increase. In this region, although the hole concentration and intragrain properties can be changed reversibly, the intergrain properties and the normal-state resistivity are not exactly reversible. This may originate from the formation of a new intergrain layer, larger than the coherence length at T_j in the overoxidation region. In this case, the possibility of a second phase formation (such as a low-T_c phase) at grain boundaries with oxygen uptake cannot be ruled out, although there is no direct experimental evidence. This reordering may also be a result of the interface growth by adsorption of excess oxygen. If this is the case, the hole concentration at the interface increases and this enhances superconductivity. On the other side, if the attractive interaction of the Cooper pairs is caused by some kind of fluctuation such as spin fluctuations[34] and/or charge fluctuations,[35] excess holes will weaken the fluctuations and interactions, causing a local weakening of superconductivity at the interface. However, a similar effect may originate from a short-range antiferromagnetic-ferromagnetic ordering due to oxygen content at the grain boundaries.[36,37]

V. CONCLUSIONS

In this study, a thermodynamic stable phase of a 110-K Bi superconductor was prepared and the hole concentration was changed in a wide range by controlling the oxygen content. The change in the hole concentration was determined by the measurements of the formal copper valency and the anisotropic Jahn-Teller effect of copper along the c direction. The oxygen uptake creates a significant chemical modification in the structure and consequently, two additional reflections were observed in the XRD pattern of all the samples. These additional peaks have also been reported by Bansal *et al.* in some multiphase $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_{10+\delta}$ samples whose lead content was between 0.0 and 0.6 (Ref. 38). The authors have proposed that the amount of Pb^{4+} ions in the BiO layers increases with the lead content and the c parameter decreases depending on the Pb^{4+} concentration. On the contrary, the photoemission studies showed that the valence of Pb in BiO layers is $+2$ and there is no evidence for Pb^{4+} (Ref. 10). The Pb addition also influences the stacking defects inside the grains of the superconducting phase.[31] Therefore, the diffusion limitations may vanish due to the lead content. In this case, the oxygen content can be raised and a decrease in the c parameter is expected. In the (Bi,Pb)-O layers, the oxygen moves off the center of a distorted (Bi,Pb) square toward a position near either one (Bi,Pb) atom (*Amma*) or two (Bi,Pb) atoms (*A*2*aa*) (Ref. 27). The off-center occupation depends on the modulation spacing which is related to the excess oxygen content. These displacements also cause the movement of the cationic positions. When the off-center occupation becomes nonrandom, a correlation of these off-center displacements will have a strong effect on the diffraction pattern. The observed additional peaks may be caused by noncentrosymmetric displacements due to excess oxygen content.

The electromagnetic properties of the samples were affected by the granular microstructure. The stepwise behavior of ac susceptibility indicates a suppression in the order parameter at grain boundaries.[12] Nevertheless, there always exists grain-boundary potential barriers in polycrystals mainly because of the lack of perfect continuity. The order parameter shifts in this region from the bulk value due to the boundary crystallography. This shift is correlated to the variation in composition within crystallographic mismatches. Although the anionic vacancy concentration can be decreased by reannealing under oxygen atmosphere, the cationic vacancy concentration cannot be controlled by such a procedure. Therefore, there always will be a suppression in the order parameter at grain boundaries. However, this suppression can be minimized in a sample with an oxygen content corresponding to the maximum value of T_c, as observed in this study. On the other hand, we observed that the midpoint temperature of resistivity transition and zero resistivity temperature are very close to the intragranular transition and the Josephson phase locking temperatures, respectively, revealing that the percolative character of carriers is closely related to the flux-pinning dynamics. This relation is also very sensitive to the inhomogeneity in local hole concentration. The kinetics of oxygen intercalation are accelerated by shifting the annealing partial pressure of oxygen and temperature to higher values and the homogeneity in local hole concentration due to oxygen content decreases. All experimental results exhibit the inhomogeneity in Josephson coupling energy and the degree of the order-parameter suppression at grain boundaries can be controlled by an annealing procedure under appropriate oxygen partial pressure. These results are very noticeable in the design of high-T_c superconductor devices.

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